Structures and Magnetic Properties of [M(cyclam)(CH₃CN)₂][Ni(dmit)₂]₂ (M = Cu, Ni) and [Cu(cyclam)]₂[2,5-DM-DCNQI]₅

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Complexes [Cu^{II}(cyclam)(CH₃CN)₂][Ni(dmit)₂]₂ (1), [Ni^{II}(cyclam)(CH₃CN)₂][Ni(dmit)₂]₂ (2), and [Cu^{II}-(cyclam)]₂[2,5-DM-DCNQI]₅ (3) (cyclam = 1,4,8,11-tetraazacyclotetradecane, dmit = isotrithionedithiolate, 2,5-DM-DCNQI = N,N'- dicyano-2,5-dimethylquinonediimine) were prepared, and crystal structures and magnetic properties have been studied. Complexes were obtained by the addition of radical salts ([But₄N][Ni(dmit)₂], Li[2,5-DM-DCNQI]₂) to [M(cyclam)](ClO₄)₂ (M = Cu, Ni) in acetonitrile. In complexes 1 and 2, coordination geometries about the metal ion in [M(cyclam)(CH₃CN)₂]²⁺ are axially distorted octahedral, where two acetonitrile molecules coordinate to the copper or nickel atoms from the axial positions, respectively. EPR measurements at 15 K and temperature-dependent magnetic susceptibilities for 1 and 2 revealed that [M(cyclam)(CH₃CN)₂]²⁺ are magnetically isolated from the radicals [Ni(dmit)₂]⁻, which form antiferromagnetically coupled dimers with the exchange coupling constants of J = –153(2) and –125.3(9) cm⁻¹ for 1 and 2, respectively. In complex 3, there are three kinds of crystallographically independent 2,5-DM-DCNQI anion radicals (A–C), where A and B coordinate to the crystallographically independent [Cu(cyclam)]²⁺, respectively. Two B's and C form a trimer (BCB), which has the formal charge of two for the trimer, and the trimers stack to build a one-dimensional chain (···BCBBCB···) whose intra- and inter-trimer separation (B–C and B–B) are 3.03–3.18 and 3.13–3.14 Å, respectively. Furthermore, the chains are linked with [Cu(cyclam)]²⁺ to form a two-dimensional network. A forms a dimer with its inverted image, and the intradimer separation is 3.71 Å. EPR measurement for 3 at 15 K showed the only axially symmetric pattern for Cu²⁺ ($g_∥$ = 2.169 and g = 2.043), and this suggests that [Cu(cyclam)]²⁺ is magnetically isolated. A slight rise in $\chi_m T$ values as temperature approached 270 K allows an estimate of $J < -400$ cm⁻¹ for the dimer (AA). Semi-empirical molecular orbital calculation for [2,5-DM-DCNQI]⁻ are presented as an aid to interpreting experiments. Crystal data: [Cu^{II}(cyclam)(CH₃CN)₂][Ni(dmit)₂]₂ (1), triclinic, space group $P\bar{1}$ with a = 11.817(4) Å, b = 12.010(4) Å, c = 9.561(4) Å, α = 115.59(2)°, β = 97.72(3)°, γ = 95.62(3)°, V = 1194.1(7) Å³, Z = 1, R = 0.065 (R_w = 0.078) for 4151 data with $|F_o| > 3\sigma(F_o)$; [Ni^{II}(cyclam)(CH₃CN)₂][Ni(dmit)₂]₂ (2), triclinic, space group $P\bar{1}$, a = 11.750(2) Å, b = 11.972(2) Å, c = 9.566(2) Å, α = 115.75(1)°, β = 96.75(2)°, γ = 96.73(1)°, V = 1182.1(7) Å³, Z = 1, R = 0.052 (R_w = 0.061) for 3671 data with $|F_o| > 3\sigma(F_o)$; [Cu^{II}(cyclam)]₂[2,5-DM-DCNQI]₅ (3), triclinic, space group $P\bar{1}$, a = 9.518(2) Å, b = 14.357(4) Å, c = 14.582(2) Å, α = 118.10(2)°, β = 91.60(2)°, γ = 90.70(2)°, V = 1756.4(8) Å³, Z = 1, R = 0.059 (R_w = 0.071) for 5864 data with $|F_o| > 3\sigma(F_o)$.

Introduction

Considerable effort has been devoted to build a molecular-based ferromagnet. Some coordination[1–3] and pure organic[4,5] compounds have been revealed to show spontaneous magnetization at very low temperature. In order to build a molecular-based

ferromagnet, it is indispensable to have three-dimensional magnetic interactions in the solids. We have been concerned with the control of intramolecular and intermolecular magnetic interaction in multinuclear and low-dimensional complexes, respectively, to establish the basic technology to build such molecular assemblies. A spin polarization mechanism[6] (topological network of dπ spins to the pπ orbitals of a bridging ligand) was applied to have a ferromagnetic interaction (J = 0.62 cm⁻¹) in a dinuclear iron(II) complex [Fe₂(bpmar)(H₂O)₄](NO₃)₄·3H₂O (H₂bpmar = 4,6-bis[N,N-bis(2-pyridylmethyl)aminomethyl]-2-methylresorcinol).[7] An orthogonal arrangement of adjacent magnetic orbitals, which stabilizes the high-spin state as a ground state, was used to have an intrachain magnetic interaction ferromagnetic (J = 1.22 cm⁻¹) in the zigzag chain copper(II) complex [Cu(bpy)(ox)]·2H₂O (bpy = bipyridine).[8] However, the magnitude of the above ferromagnetic interactions seems not to be big enough to attain ferromagnetism even if the magnetic interaction can be extended to a three-dimensional system.

In the development of organic conductors, the construction of multidimensional electronic interactions in molecular solids has been an intensive subject to avoid a ubiquitous metal-to-insulator transition, which arises from the instability of one-dimensionality, the so-called Peierls transition.[9] Some organic radical systems are known to retain their metallic characteristics down to very

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low temperature,[10] and these solids have a fairly strong electronic interaction through their network system. If a paramagnetic metal complex is introduced into the radical network as a component, such molecular assemblies are expected to have interesting physical properties like a molecular ferro- or ferrimagnetic metal. $Ni(dmit)_2$ (dmit = isotrithionedithiolate)[11] and disubstituted DCNQI (=dicyanoquinonediimine)[12] salts have been reported to be metallic even at very low temperatures as a results of their multidimensional electronic interaction, and some inorganic salts have been revealed to be superconductors. Macrocyclic ligand cyclam (1,4,8,11-tetraazacyclotetradecane) forms a variety of metal complexes $[M(cyclam)]^{n+}$ in which the metal ion has one or two available coordination sites in addition to the four occupied coordination sites from the cyclam. If the organic radicals coordinate to $[M(cyclam)]^{n+}$, the metal complex can be assembled into a multidimensional network system shown as follows:

conduction column   metal complex   conduction column
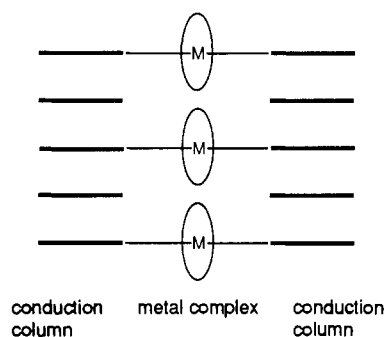
In this paper, copper(II) and nickel(II) complexes with organic radicals $[Ni(dmit)]^-$ or $[2,5-DM-DCNQI]^{r-}$ were prepared and their crystal structures and magnetic properties were studied.

Experimental Section

Syntheses. All chemicals used were commercially available and used without further purification. $[M(cyclam)](ClO_4)_2$ (M = Cu, Ni),[13] $[Bu_4N][Ni(dmit)_2]$,[14] and $Li[2,5-DM-DCNQI]_2$[15] were prepared by the literature methods. All procedure were carried out in an inert atmosphere.

$[M(cyclam)(CH_3CN)_2][Ni(dmit)_2]_2$ (M = Cu, Ni) and $[Cu(cyclam)]_2$-$[2,5-DM-DCNQI]_5$. To a hot acetonitrile solution (200 mL) of $[Bu_4N]$-$[Ni(dmit)_2]$ or $Li[2,5-DM-DCNQI]_2$ was added an acetonitrile solution of $[M(cyclam)](ClO_4)_2$. After the solution was left standing overnight, black crystallines were formed and one of them was subjected to the

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Table I. Crystallographic Data for $[Cu(cyclam)(CH_3CN)_2][Ni(dmit)_2]_2$ (**1**), $[Ni(cyclam)(CH_3CN)_2][Ni(dmit)_2]_2$ (**2**), and $[Cu(cyclam)]_2[2,5-DM-DCNQI]^5$ (**3**)

	1	2	3
formula	$C_{26}H_{30}CuN_6Ni_2S_{20}$	$C_{26}H_{30}N_6Ni_3S_{20}$	$C_{70}H_{88}N_{28}Cu_2$
fw	1248.71	1243.86	1448.74
temp (°C)	22	22	22
cryst system	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	11.817(4)	11.750(2)	9.518(2)
b (Å)	12.010(4)	11.972(2)	14.357(4)
c (Å)	9.561(4)	9.566(2)	14.582(2)
α (deg)	115.59(2)	115.75(1)	118.10(2)
β (deg)	97.72(3)	96.75(2)	91.60(2)
γ (deg)	95.62(3)	96.73(1)	90.70(2)
V (Å³)	1194.1(7)	1182.1(5)	1756.4(8)
Z	1	1	1
D_c (g cm⁻³)	1.736	1.747	1.462
radiation λ (Mo Kα) (Å)	0.710 73	0.170 73	0.710 73
μ(Mo Kα)(cm⁻¹)	21.0	20.5	7.2
transm coeff	0.501–0.928	0.626–0.935	0.816–0.965
no. of reflcns measd	6265	6019	5984
no. of reflcns obsd	4151	3671	5603
R^a	0.065	0.052	0.059
R_w^b	0.078	0.061	0.070

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = (\sigma_c^2 + (0.020|F|^2)^{-1}$ for **1**, $w = (\sigma_c^2 + (0.025|F|^2)^{-1}$ for **2**, and $w = (\sigma_c^2 + (0.030|F|^2)^{-1}$ for **3**.

X-ray analysis. Anal. Calcd for $C_{26}H_{30}CuN_6Ni_2S_{20}$ (**1**): C, 25.01; H, 2.42; N, 6.73. Found: C, 25.17; H, 2.42; N, 6.73. Anal. Calcd for $C_{26}H_{30}CuN_6Ni_2S_{20}$ (**2**): C, 25.11; H, 2.43; N, 6.76. Found: C, 25.20; H, 2.52; N, 6.81. Anal. Calcd for $C_{70}H_{88}Cu_2N_8$ (**3**): C, 58.03; H, 6.12; N, 27.07. Found: C, 57.61; H, 6.18; N, 26.83.
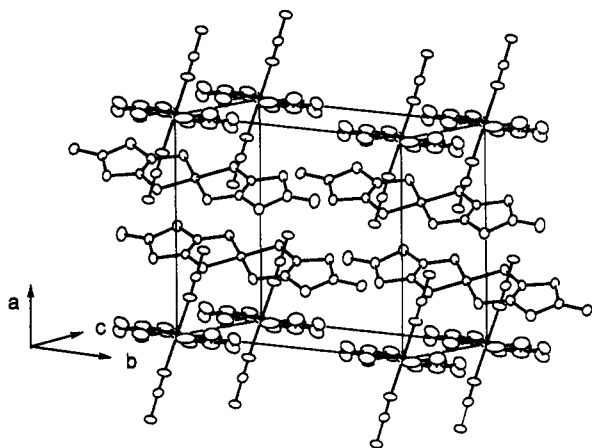
Magnetic Measurement. Temperature-dependent magnetic susceptibilities of powdered samples were measured by an Oxford Faraday type magnetic balance system. All data were corrected for diamagnetism.[16] Temperature readings were calibrated with a magnetic thermometer by use of $[Cr(NH_3)_6]Cl_3$. EPR spectra were recorded on a JEOL FE2XG spectrometer operating at X-band frequencies with a magnetic field modulation of 100 kHz. Microwave frequency was measured with a Takeda Riken 5201 frequency counter, and the magnetic field values of the signals were measured with an Echo Denshi EFM 200.

Molecular Orbital Calculations. The semi-empirical molecular orbital calculation MNDO method[17] was used for the $[DCNQI]^-$ molecule. Geometrical parameters were taken from the X-ray structural data.

X-ray Crystallography. Black, tabular crystals of **1–3** (dimensions 0.48 × 0.40 × 0.04, 0.40 × 0.32 × 0.05, and 0.68 × 0.50 × 0.04 mm, respectively) were mounted on a glass fiber and coated with epoxy to retard possible solvent loss. Data were collected at 295 K on Rigaku AFC5R and Enraf-Nonius CAD-4 diffractometers using the ω-2θ scan technique to a maximum $2\theta = 55, 55$, and 60° for **1–3**, respectively. Unit cell parameters were obtained by least-square refinement of 25 accurate centered reflections having $12 < \theta < 15°$. Crystallographic data and data collection parameters are summarized in Tables I and SI–SIII (supplementary material). The stabilities of the crystals were monitored every 100 reflections using three standard reflections, and no significant decay in the intensities of these reflections was observed. Corrections were applied for Lorentz–polarization and absorption effects but not for extinction. Scattering factors were taken from ref 18, and anomalous dispersion effects were included in F_c.[19] The structures were solved by the conventional heavy-atom method followed by the standard difference Fourier routines. Refinement of non-hydrogen atoms with anisotropic temperature factors was done by the block-diagonal least-squares method, and hydrogen atoms found in the difference Fourier maps were included

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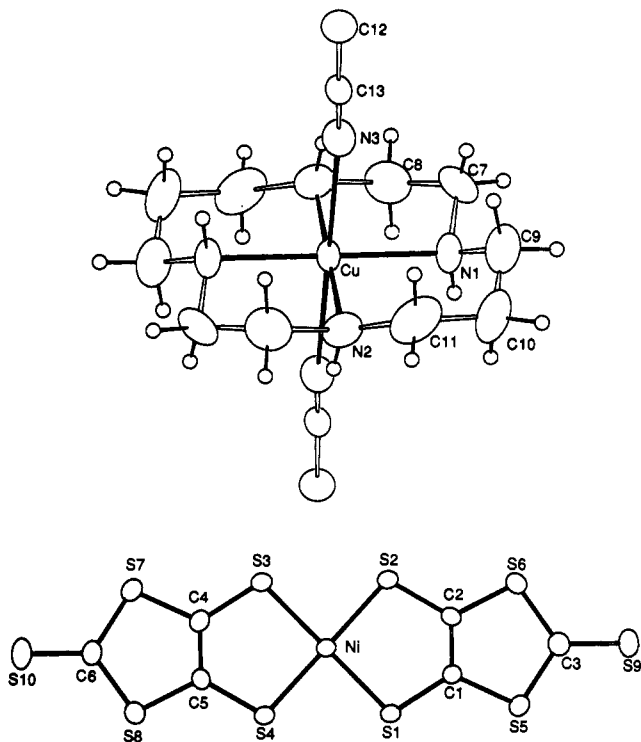
Figure 1. ORTEP drawing of [Cu(cyclam)(CH3CN)2][Ni(dmit)2]2.

Figure 2. Packing diagram of [Cu(cyclam)(CH3CN)2][Ni(dmit)2]2.

Table II. Positional ($\times 10^4$) and Equivalent Isotropic Thermal Parameters (Å^2) for [Cu(cyclam)(CH3CN)2][Ni(dmit)2]2 (1)

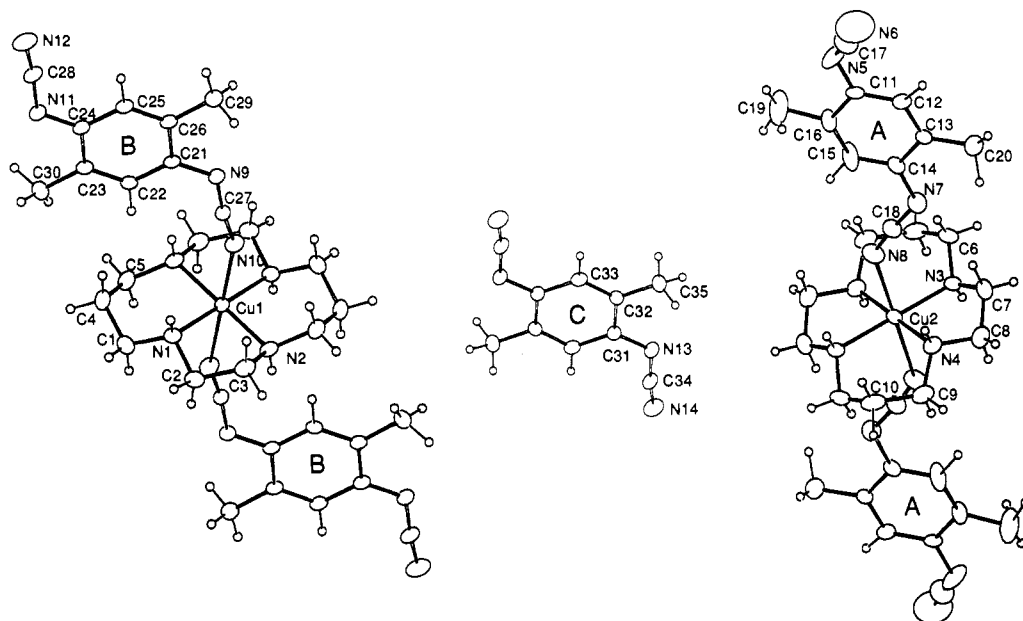|	x	y	z	$B_{eq}{}^a$
Cu	0	0	0	3.9
Ni	3316(1)	1007(1)	5042(1)	2.7
S(1)	3946(1)	2480(1)	4471(2)	3.5
S(2)	2565(1)	2236(1)	6950(2)	3.6
S(3)	2709(1)	−471(1)	5619(2)	3.6
S(4)	3974(1)	−239(1)	3051(2)	3.3
S(5)	3699(1)	5218(1)	5881(2)	3.8
S(6)	2357(1)	4971(1)	8059(2)	4.0
S(7)	2686(1)	−3267(1)	3946(2)	3.9
S(8)	3976(1)	−3029(1)	1701(2)	3.8
S(9)	2813(1)	7445(1)	8033(2)	4.6
S(10)	3318(2)	−5548(2)	1528(2)	5.9
N(1)	571(4)	295(7)	2250(7)	6.0
N(2)	−139(5)	1832(7)	969(8)	5.8
C(1)	3459(4)	3740(5)	5804(6)	2.8
C(2)	2857(5)	3631(5)	6869(6)	3.0
C(3)	2933(5)	5951(5)	7353(7)	3.3
C(4)	3061(5)	−1756(5)	4174(6)	3.0
C(5)	3630(5)	−1654(5)	3071(6)	3.0
C(6)	3328(5)	−4033(5)	2340(7)	3.7
C(7)	269(7)	1547(10)	3275(8)	7.8
C(8)	497(8)	2431(9)	2580(12)	7.9
C(9)	172(7)	−641(11)	2653(11)	7.9
C(10)	477(8)	−1841(10)	1684(13)	8.2
C(11)	156(8)	2572(9)	118(15)	8.5
N(S)	2059(5)	551(6)	−126(7)	5.5
C(S1)	4197(5)	1391(7)	118(9)	4.9
C(S2)	2990(5)	922(6)	−20(6)	3.7

^{a} The equivalent isotropic temperature factor is calculated using the expression $B_{eq} = (4/3)\omega_i\omega_j a_i a_j \beta_{ij}$, where a_i's are the unit cell edges in direct space.

Table III. Positional ($\times 10^4$) and Equivalent Isotropic Thermal Parameters (Å^2) for [Ni(cyclam)(CH3CN)2][Ni(dmit)2]2 (2)

	x	y	z	B_{eq}
Ni(1)	0	0	0	3.8
Ni(2)	3326(1)	981(1)	4970(1)	2.8
S(1)	3954(1)	2462(1)	4389(2)	3.5
S(2)	2571(1)	2209(1)	6893(2)	3.7
S(3)	2696(1)	−514(1)	5535(2)	3.6
S(4)	4022(1)	−259(1)	2999(2)	3.3
S(5)	3737(1)	5220(1)	5833(2)	3.8
S(6)	2408(1)	4971(1)	8059(2)	4.1
S(7)	2698(1)	−3316(1)	3877(2)	4.0
S(8)	4048(1)	−3052(1)	1664(2)	3.9
S(9)	2928(1)	7478(1)	8080(2)	4.9
S(10)	3393(2)	−5589(1)	1487(2)	5.9
N(1)	571(4)	341(6)	2294(6)	6.2
N(2)	−165(4)	1874(6)	989(7)	6.5
C(1)	3479(4)	3734(4)	5747(6)	2.9
C(2)	2868(4)	3619(5)	6813(6)	3.3
C(3)	3001(4)	5959(5)	7344(6)	3.6
C(4)	3073(4)	−1803(5)	4091(6)	3.1
C(5)	3678(4)	−1676(4)	3020(5)	2.9
C(6)	3388(5)	−4066(5)	2301(6)	3.7
C(7)	251(6)	1599(9)	3298(7)	7.6
C(8)	465(7)	2481(8)	2575(10)	8.0
C(9)	169(6)	−568(10)	2721(10)	8.1
C(10)	491(7)	−1803(9)	1699(11)	8.0
C(11)	133(7)	2618(9)	146(13)	9.2
N(S)	1773(4)	535(5)	−117(6)	4.5
C(S1)	3977(4)	1201(6)	−27(7)	4.3
C(S2)	2735(4)	824(5)	−81(6)	3.4

in the refinement with isotropic temperature factors with use of the standard programs.[20] The refinements minimized the function $\Sigma w(|F_o| - |F_c|)^2$, where $w = [\sigma^2(F) + (0.020|F_o|)^2]^{-1}$ for **1**, $w = [\sigma^2(F) + (0.025|F_o|)^2]^{-1}$ for **2**, and $w = [\sigma^2(F) + (0.030|F_o|)^2]^{-1}$ for **3** and converged to the *R* factors reported in Table I. The largest peak in the final difference Fourier map had 0.94, 0.98, and 0.72 e/Å^3 for **1–3**, respectively.

Results and Discussion

Description of Structures. [Cu(cyclam)(CH3CN)2][Ni(dmit)2]2 (**1**) and [Ni(cyclam)(CH3CN)2][Ni(dmit)2]2 (**2**). Crystals **1** and **2** are isomorphous to each other. The ORTEP for **1** and packing diagrams for **2** are shown in Figures 1 and 2, respectively. Atomic parameters for **1** and **2** are listed in Tables II and III, and Tables V and VI list selected interatomic distances and angles.

In **1**, the copper atom on the inversion center is bound in distorted octahedral fashion of which four nitrogen atoms from cyclam and two nitrogen atoms from solvent molecules occupy the equatorial and axial sites, respectively. Bond distances between copper and coordinated atoms are 2.028(7)–2.019(7) Å for equatorial and 2.491(6) Å for axial nitrogen atoms. The

(20) Sakurai, T.; Kobayashi, K. *Sci. Rep. Inst. Chem. Phys. Res. (Jpn.)* **1979**, *55*, 69.

axial bond (Cu–N(acetonitrile)) is tilted 2.1(2)° with respect to the right angle of the equatorial plane. The nickel atom in the anion is coordinated by four sulfur atoms, and the coordination geometry about the nickel atom is a square plane. The dihedral angle between the two dmit ligands is 1.50(6)°, and the nickel atoms stay 0.02(1) Å above the S4 plane. Intermolecular S···S contacts are in the range 3.026(2)–3.687(3) Å, where the sum of van der Waals radii of the sulfur atoms is 3.60 Å.[21] It can be concluded that the anion [Ni(dmit)2]⁻ forms a dimer with its

Figure 3. ORTEP drawing of [Cu(cyclam)]₂[2,5-DMDCNQI]₅.

Table IV. Positional (×10⁴) and Equivalent Isotropic Thermal Parameters (Å²) for [Cu(cyclam)]₂[2,5-DM-DCNQI]₅ (3)

	x	y	z	B_{eq}		x	y	z	B_{eq}
Cu(1)	10000	0	5000	2.5	C(17)	1732(7)	11792(4)	11692(4)	6.9
Cu(2)	5000	5000	5000	3.6	C(18)	4251(5)	7359(3)	7114(3)	4.8
N(1)	11804(3)	−24(2)	5760(2)	2.9	C(19)	645(11)	8837(4)	9945(6)	15.2
N(2)	11239(3)	−332(2)	3778(2)	2.9	C(20)	5150(4)	10571(3)	8562(4)	5.1
N(3)	4839(3)	4032(2)	5652(2)	3.3	N(9)	9247(3)	−3741(2)	3117(2)	2.6
N(4)	3030(3)	4482(2)	4421(2)	3.6	N(10)	9600(3)	−1866(2)	4371(2)	3.6
C(1)	11708(4)	−493(3)	6457(3)	3.8	N(11)	7992(3)	−5443(2)	−1082(2)	2.9
C(2)	12861(4)	−524(3)	4969(3)	3.4	N(12)	7776(4)	−7366(3)	−2257(3)	4.6
C(3)	12703(4)	−128(3)	4188(3)	3.6	C(21)	8957(3)	−4126(2)	2088(2)	2.2
C(4)	10891(4)	184(3)	3144(3)	4.0	C(22)	8805(3)	−3506(2)	1577(2)	2.3
C(5)	9384(5)	−41(3)	2725(3)	4.3	C(23)	8497(3)	−3911(2)	545(2)	2.3
C(6)	6112(5)	3468(3)	5681(3)	4.8	C(24)	8304(3)	−5053(2)	−68(2)	2.4
C(7)	3608(5)	3321(3)	5139(3)	4.4	C(25)	8454(3)	−5666(2)	456(2)	2.6
C(8)	2463(4)	3951(3)	4993(3)	4.3	C(26)	8788(3)	−5249(2)	1486(2)	2.4
C(9)	2071(4)	5264(4)	4391(3)	4.8	C(27)	9424(3)	−2727(2)	3729(2)	2.5
C(10)	2646(5)	5778(4)	3790(4)	5.6	C(28)	7880(3)	−6484(3)	−1677(3)	3.2
N(5)	1266(5)	10950(3)	10895(4)	8.9	C(29)	8994(4)	−5907(3)	2021(3)	3.5
N(6)	2072(8)	12530(5)	12395(4)	12.4	C(30)	8354(4)	−3230(3)	34(3)	3.2
N(7)	4543(4)	8379(3)	7603(3)	5.4	N(13)	14370(3)	3908(2)	7892(2)	2.8
N(8)	4086(5)	6460(3)	6628(3)	5.6	N(14)	13866(4)	1980(3)	6939(3)	4.5
C(11)	2105(3)	10335(2)	10090(3)	3.1	C(31)	14694(3)	4416(2)	8915(2)	2.4
C(12)	3183(4)	10727(3)	9738(3)	4.1	C(32)	14883(3)	5550(2)	9404(2)	2.4
C(13)	4000(3)	10115(3)	8919(3)	3.0	C(33)	14846(3)	3917(2)	9554(3)	2.7
C(14)	3702(5)	9030(3)	8427(3)	4.0	C(34)	14128(3)	2872(3)	7431(2)	3.1
C(15)	2627(7)	8648(3)	8777(4)	8.2	C(35)	14794(4)	6097(3)	8757(3)	3.3
C(16)	1821(5)	9276(3)	9601(3)	5.2					

Table V. Selected Bond Lengths (Å) and Bond Angles (deg) for [Cu(cyclam)(CH₃CN)₂][Ni(dmit)₂]₂ (1)ᵃ

Cu–N(1)	2.028(7)	Cu–N(2)	2.019(7)
Cu–N(S)	2.491(6)	Ni–S(1)	2.160(2)
Ni–S(2)	2.158(2)	Ni–S(3)	2.161(2)
Ni–S(4)	2.153(2)		

N(1)–Cu–N(2)	85.8(3)	N(1)–Cu–N(S)	87.7(2)
N(1)–Cu–N(2)*	94.2(3)	N(1)–Cu–N(S)*	92.3(2)
N(2)–Cu–N(S)	90.3(2)	N(2)–Cu–N(S)*	89.7(2)
S(1)–Ni–S(2)	93.61(7)	S(1)–Ni–S(3)	179.23(7)
S(1)–Ni–S(4)	86.38(7)	S(2)–Ni–S(3)	86.80(7)
S(2)–Ni–S(4)	176.79(7)	S(3)–Ni–S(4)	93.24(7)

ᵃ An asterisk indicates part of symmetry operation 1 − x, 1 − y, 1 − z.

inversion image as seen in the packing diagram (Figure 2). Interplanar distances in the two [Ni(dmit)₂]⁻ molecules are in the range 3.49–3.90 Å.

Table VI. Selected Bond Lengths (Å) and Bond Angles (deg) for [Ni(cyclam)(CH₃CN)₂][Ni(dmit)₂]₂ (2)ᵃ

Ni(1)–N(1)	2.060(6)	Ni(1)–N(2)	2.065(7)
Ni(1)–N(S)	2.137(5)	Ni(2)–S(1)	2.156(2)
Ni(2)–S(2)	2.161(2)	Ni(2)–S(3)	2.161(2)
Ni(2)–S(4)	2.155(2)		

N(1)–Ni(1)–N(2)	85.1(3)	N(1)–Ni(1)–N(S)	88.1(2)
N(1)–Ni(1)–N(2)*	94.9(3)	N(1)–Ni(1)–N(S)*	91.9(2)
N(2)–Ni(1)–N(S)	89.9(2)	N(2)–Ni(1)–N(S)*	90.1(2)
S(1)–Ni(2)–S(2)	93.61(6)	S(1)–Ni(2)–S(3)	179.56(5)
S(1)–Ni(2)–S(4)	86.42(6)	S(2)–Ni(2)–S(3)	86.79(7)
S(2)–Ni(2)–S(4)	178.03(6)	S(3)–Ni(2)–S(4)	93.18(6)

ᵃ See footnote a of Table V.

In **2**, the coordination geometry about the nickel atom in the cation is close to octahedral with the average bond distances of 2.063(6) and 2.157(7) Å for Ni(1)–N(cyclam) and Ni(1)–N(3)-(CH₃CN) and the axial bond (Ni–N(acetonitrile)) is tilted 1.6-(2)° with respect to the right angle of the equatorial plane. The molecular geometries of the anions are identical with those of **1**,
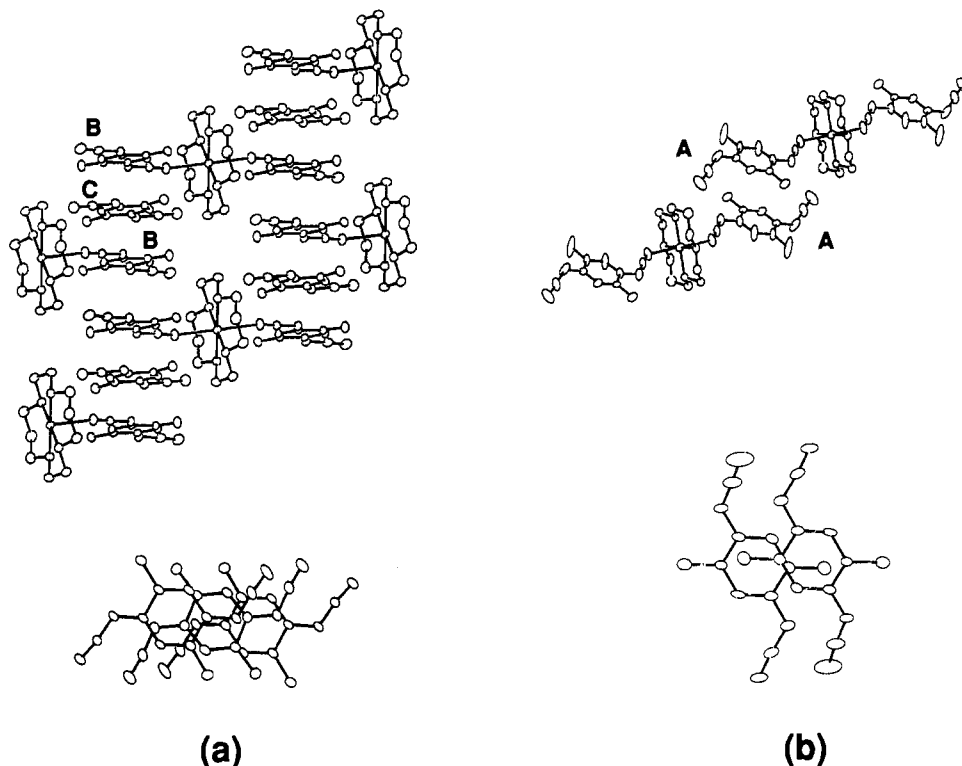
(21) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

Figure 4. Stacking diagram of [Cu(cyclam)]₂[2,5-DMDCNQI]₅: (a) **BCB** and (b) **AA** stacks.

and the anion radicals form a dimer with an intradimer distance of 3.53–3.79 Å. In a series of [Ni(dmit)₂]ⁿ⁻, intramolecular bond distances reflect the electronic nature of the radical. Interatomic distances for **1** show bond lengths different from those for [Ni-(dmit)₂]Xᵧ (X = n-Bu₄N, y = 0.29;²² X = Et₄N, y = 0.5²³), which are in the mixed-valence state. For example, all interatomic bond lengths except for the C(1)–C(2) and S(9)–C(3) bonds for the anions of **1** and **2** are 0.017–0.025 Å longer than those for (Et₄N)₀.₅-[Ni(dmit)₂],²³ whose formal charge is ¹/₂ for the [Ni(dmit)₂] unit. On the other hand, the interatomic bond distances of the anions of **1** and **2** are in good accord with the values found for [N(C₄H₉)₄][Ni(dmit)₂],²⁴ which is regarded as a monoanion radical. It is reasonable to conclude that the [Ni(dmit)₂] molecules in **1** and **2** are monoanionic.

[Cu(cyclam)]₃[2,5-DM-DCNQI]₅ (3). ORTEP drawings of **3** with numbering schemes are shown in Figure 3. Crystallographic data, positonal parameters for non-hydrogen atoms, and selected bond lengths and angles are respectively listed in Tables I, IV, and VII. The black crystal consists of two and three kinds of crystallographically independent [Cu(cyclam)]²⁺ and [2,5-DM-DCNQI]ⁿ⁻ (called **A**, **B**, and **C**) molecules, respectively, where **A** and **B** coordinate to [Cu(cyclam)]²⁺. Two copper atoms are located on the center of symmetry and coordination geometries of each copper atom are axially distorted octahedron. The equatorial plane of the copper atom consists of four nitrogen atoms of cyclam, and two axial positions are occupied by the nitrogen atoms of 2,5-DM-DCNQI (**A** or **B**). The bond lengths between the copper and equatorial nitrogen atoms (2.017(3)–2.031(3) Å) are shorter than those for axial bonds (2.410(3)–2.502(3) Å). The ground states (magnetic orbital) of the copper atoms are dₓ²₋ᵧ², which is on the equatorial plane. **C** on the inversion center forms a trimer with two **B**'s, which are related to each other by inversion (Figure 4a). The overlap of the 2,5-DM-DCNQI molecules within the trimer (**BCB**) is of usual "ring
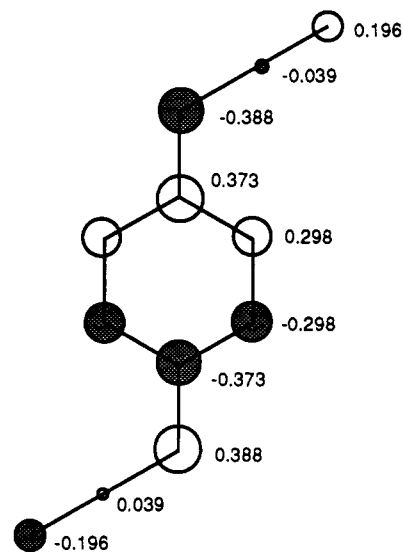
(22) Valade, L.; Legros, J.-P.; Bousseau, M.; Cassoux, P.; Garbauskas, M.; Interrante, L. V. *J. Chem. Soc., Dalton Trans.* **1985**, 783.
(23) Kato, R.; Kobayashi, H.; Kobayashi, A.; Sasaki, Y. *Chem. Lett.* **1984**, 1.
(24) Lindqvist, O.; Andersen, L.; Sieler, J.; Steimecke, G.; Hoyer, E. *Acta Chim. Scand.* **1982**, *A36*, 854.

Figure 5. MNDO diagram of the SOMO of [DCNQI]⁻.

over bond" type, and the trimers stack to form a one-dimensional structure (···**BCBBCB**···). It should be noted that the one-dimensional chains are linked by the [Cu(cyclam)]²⁺ to form a two-dimensional network. The interplanar distance between the **B** and **C** is in the range 3.03–3.18 Å, and that between two **B**'s is in the range 3.13–3.14 Å. On the other hand, two **A**'s, which are related by inversion, form a dimer with an interplanar distance of 3.71 Å, and each component of the dimer coordinates to [Cu-(cyclam)]²⁺. As a result, the dimers form a one-dimensional chain (Figure 4b).

Interatomic distances of the DCNQI's can suggest the formal oxidation number of the molecule and different bond lengths can be interpreted by the virtue of a molecular orbital calculation. Principal bond lengths of the anions are listed together with other DCNQI molecules²⁵ in Table VIII. Interatomic bond lengths of **B** show the same values as **C**, so the formal charges of **B** and **C** are considered to be identical to each other. Comparison of bond lengths of **B** or **C** with **A** clearly reveals the bonds a and c to be

Table VII. Selected Bond Lengths (Å) and Bond Angles (deg) for [Cu(cyclam)]₂[2,5-DM-DCNQI]₅ (3)[a]

		Cation	
Cu(1)-N(1)	2.027(3)	Cu(1)-N(2)	2.031(3)
Cu(1)-N(10)	2.410(3)	Cu(2)-N(3)	2.026(4)
Cu(2)-N(3)	2.017(3)	Cu(2)-N(8)	2.502(3)
N(1)-Cu(1)-N(2)	85.2(1)	N(1)-Cu(1)-N(10)	91.0(1)
N(2)-Cu(1)-N(10)	89.3(1)	N(3)-Cu(2)-N(4)	85.6(1)
N(3)-Cu(2)-N(8)	88.7(1)	N(4)-Cu(2)-N(8)	91.4(1)
Cu(1)-N(1)-C(1)	116.6(2)	Cu(1)-N(1)-C(2)	106.9(2)
Cu(1)-N(2)-C(3)	106.9(2)	Cu(1)-N(2)-C(4)	116.3(2)
Cu(1)-N(10)-C(27)	153.9(3)	Cu(2)-N(3)-C(6)	117.0(3)
Cu(2)-N(3)-C(7)	106.7(3)	Cu(2)-N(4)-C(8)	107.0(2)
Cu(2)-N(4)-C(9)	116.8(3)	Cu(2)-N(8)-C(18)	137.7(4)
Cu(2)-N(8)-C(18)	137.7(4)		
		Conformer A	
N(5)-C(11)	1.374(6)	N(5)-C(17)	1.282(6)
N(6)-C(17)	1.109(7)	N(7)-C(14)	1.405(5)
N(7)-C(18)	1.313(5)	N(8)-C(18)	1.149(5)
C(11)-C(12)	1.385(6)	C(11)-C(16)	1.361(5)
C(12)-C(13)	1.372(5)	C(13)-C(14)	1.395(5)
C(13)-C(20)	1.495(7)	C(14)-C(15)	1.373(8)
C(15)-C(16)	1.376(7)	C(16)-C(19)	1.487(11)
C(11)-N(5)-C(17)	122.4(5)	C(14)-N(7)-C(18)	118.4(4)
N(5)-C(11)-C(12)	124.4(3)	N(5)-C(11)-C(16)	116.8(4)
C(12)-C(11)-C(16)	118.8(3)	C(11)-C(12)-C(13)	124.3(3)
C(12)-C(13)-C(14)	116.4(4)	C(12)-C(13)-C(20)	122.6(3)
C(14)-C(13)-C(20)	121.1(3)	N(7)-C(14)-C(13)	117.8(3)
N(7)-C(14)-C(15)	123.2(3)	C(13)-C(14)-C(15)	119.0(3)
C(14)-C(15)-C(16)	123.7(4)	C(11)-C(916)-C(15)	117.8(5)
C(11)-C(16)-C(19)	119.9(4)	C(15)-C(16)-C(19)	122.3(4)
N(5)-C(17)-N(6)	176.7(8)	N(7)-C(18)-N(8)	174.0(5)
		Conformer **B**	
N(9)-C(21)	1.350(4)	N(9)-C(27)	1.306(4)
N(10)-C(27)	1.152(4)	N(11)-C(24)	1.334(4)
N(11)-C(28)	1.330(4)	N(12)-C(28)	1.145(4)
C(21)-C(22)	1.412(6)	C(21)-C(26)	1.431(4)
C(22)-C(23)	1.354(5)	C(23)-C(24)	1.457(4)
C(23)-C(30)	1.488(6)	C(24)-C(25)	1.418(6)
C(25)-C(26)	1.356(5)	C(26)-C(29)	1.494(6)
C(21)-N(9)-C(27)	121.1(3)	C(24)-N(11)-C(28)	119.2(4)
N(9)-C(21)-C(22)	124.9(3)	N(9)-C(21)-C(26)	116.6(3)
C(22)-C(21)-C(26)	118.4(3)	C(21)-C(22)-C(23)	123.8(3)
C(22)-C(23)-C(24)	117.9(4)	C(22)-C(23)-C(30)	122.2(3)
C(24)-C(23)-C(30)	119.9(3)	N(11)-C(24)-C(23)	117.4(4)
N(11)-C(24)-C(25)	124.8(3)	C(23)-C(24)-C(25)	117.8(3)
C(24)-C(25)-C(26)	123.5(3)	C(21)-C(26)-C(25)	118.5(4)
C(21)-C(26)-C(29)	118.5(3)	C(25)-C(26)-C(29)	123.0(3)
N(9)-C(27)-N(10)	171.2(5)	N(11)-C(28)-N(12)	174.5(5)
		Conformer C	
N(13)-C(31)	1.341(4)	N(13)-C(34)	1.326(4)
N(14)-C(34)	1.155(5)	C(31)-C(32)	1.444(4)
C(31)-C(33)	1.423(6)	C(32)-C(33)*	1.356(4)
C(32)-C(35)	1.486(6)		
C(31)-N(13)-C(34)	118.9(4)	N(13)-C(31)-C(32)	117.6(4)
N(13)-C(31)-C(33)	124.6(3)	C(32)-C(31)-C(33)	117.8(3)
C(31)-C(32)-C(33)*	118.5(4)	C(33)*-C(32)-C(35)	121.9(3)
C(31)-C(32)-C(35)	119.5(3)	C(31)-C(33)-C(32)*	123.6(3)
N(13)-C(34)-N(14)	172.8(5)		

[a] An asterisk indicates part of symmetry operation 3 − x, 1 − y, 2 − z.

longer for **A** and bonds b and d to be shorter for **A** (see Table VIII). A MNDO molecular orbital calculation for DCNQI⁻ was done, and its SOMO (singly occupied molecular orbital) was depicted in Figure 5. Bonds like a and c with an antibonding character should be lengthened as the negative charge of the molecule is increased, while a bond like b with a bonding character should be shortened. And a bond like e with small orbital coefficients should not be changed much. Hence, the formal charges for **B** and **C**, which are identical to each other, should be smaller than that for **A**. Total number of charges (or spins)
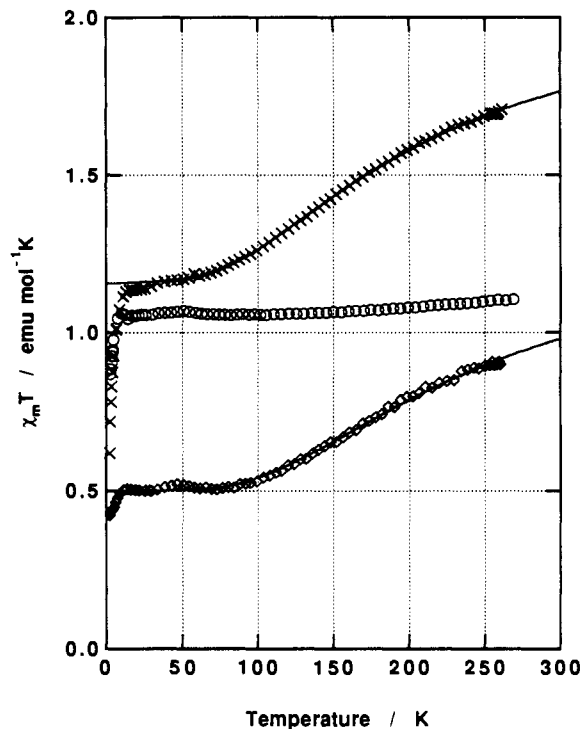
(25) (a) Andreetti, G. D.; Bradamante, S.; Bizzarri, P. C.; Pagani, G. A. *Mol. Cryst. Liq. Cryst.* **1985**, *120*, 309. (b) Kato, R.; Kobayashi, H.; Kobayashi, A.; Mori, T.; Inokuchi, H. *Synth. Met.* **1988**, *27*, B263.

Figure 6. Temperature dependence of $\chi_m T$ for (◇) [Cu(cyclam)-(CH₃CN)₂][Ni(dmit)₂]₂, (✕) [Ni(cyclam)(CH₃CN)₂][Ni(dmit)₂]₂, and (○) [Cu(cyclam)]₂[2,5-DMDCNQI]₅. Solid lines result from a least-squares fit using the parameters and equations described in the text.

for the anions is four because there are two [Cu(cyclam)(CH₃-CN)₂]²⁺ molecules. The cations have trimer (**BCB**) and dimer (**AA**) as the counteranions, respectively, so the four negative charges (or spins) can be divided into two each for the trimer and dimer. That is to say, the formal charges for **B**, **C**, and **A** are $-^2/_3$, $-^2/_3$, and −1, respectively. The tendency of bond length changes with different negative charges is in good accord with other DCNQI's (Table VIII).

Magnetic Properties. Variable-temperature magnetic susceptibility data were collected down to 2.5 K, and $\chi_m T$ versus temperature plots were depicted in Figure 6, where χ_m is the molar magnetic susceptibility.
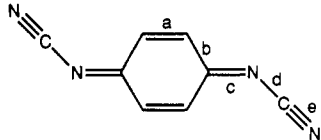
[Cu(cyclam)(CH₃CN)₂][Ni(dmit)₂]₂ (1). Complex **1** has $\chi_m T$ values steadily decrease from 0.90 emu mol⁻¹ K at 260 K down to 0.50 emu mol⁻¹ K at 80 K, whereupon the values do not change down to 14 K. EPR spectra (Figure 7a of a powdered sample **1** at 15 K show only axially symmetric signal ($g_\parallel$ = 2.169 and g = 2.043) for copper(II) ion without a triplet signal for the [Ni(dmit)₂]⁻ dimer. This suggests that the [Cu(cyclam)(CH₃-CN)₂]²⁺ is magnetically isolated from [Ni(dmit)₂]⁻ ions, whereas the antiferromagnetic coupling between the components of the [Ni(dmit)₂]⁻ dimer must be fairly strong to be diamagnetic at 15 K. The magnetic susceptibility data for **1** were fit to the sum (eq 1) of the Curie and Bleaney–Bowers[26] equations for

$$\chi_m = \frac{N g_{Cu}^2 \beta^2}{4kT} + \frac{N g^2 \beta^2}{kT}\left[\frac{2}{3 + \exp(-2J/kT)}\right] + N\alpha \quad (1)$$

[Cu(cyclam)(CH₃CN)₂]²⁺ and the [Ni(dmit)₂]⁻ dimer, respectively. N, g_{Cu}, g, β, k, and J represent Avogadro's number, the g value for copper, the g value for [Ni(dmit)₂]⁻, a Bohr magnetron, and the Boltzmann and exchange coupling constants for the [Ni(dmit)₂]⁻ dimer, respectively. The temperature-independent

(26) Bleaney, B.; Bowers, K. D. *Proc. R. Soc. London, Ser. A* **1952**, *214*, 451.

Table VIII. List of Bond Lengths of DCNQI Series with Different Formal Charges

compd	a	b	c	d	e	formal charge
DCNQI	1.336(2)	1.450(2)	1.303(2)	1.334(2)	1.150(2)	neutral[a]
		1.446(2)				
Cu[2,5-DM-DCNQI]₂	1.350(6)	1.433(6)	1.342(6)	1.312(6)	1.159(6)	$-^1/_2$[b]
Li[2,5-DM-DCNQI]₂			1.323(3)	1.328(3)	1.145(3)	$-^1/_2$[c]
conformer **B**	1.356(5)	1.431(4)	1.350(4)	1.306(4)	1.152(4)	$-^2/_3$
	1.354(5)	1.412(6)	1.334(4)	1.330(4)	1.145(4)	
conformer **C**	1.356(4)	1.444(4)	1.341(4)	1.326(4)	1.155(5)	$-^2/_3$
		1.423(6)				
conformer **A**	1.376(7)	1.361(5)	1.374(6)	1.282(6)	1.109(7)	-1
	1.372(5)	1.385(6)	1.405(5)	1.313(5)	1.140(5)	

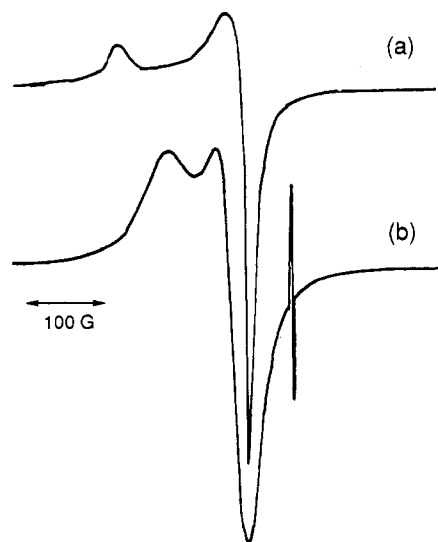[a] Reference 25a. [b] Reference 12c. [c] Reference 25b.

Figure 7. EPR spectra of powdered sample at 15 K for (a) [Cu-(cyclam)(CH₃CN)₂][Ni(dmit)₂]₂ and (b) [Cu(cyclam)]₂[2,5-DMDC-NQI]₅.

paramagnetism, $N\alpha$, was taken as 60×10^{-6} emu/Cu. The best fit of eq 1 was obtained with $J = -153(2)$ cm⁻¹, $g_{Cu} = 2.253(6)$, and $g = 2.08(2)$, where the data above 70 K were used to the calculation.

[Ni(cyclam)(CH₃CN)₂][Ni(dmit)₂]₂ (2). $\chi_m T$ values for **2** show the same temperature dependence as **1**, although the $\chi_m T$ values vary from 1.70 emu mol⁻¹ K at 262 K to 1.18 emu mol⁻¹ K at 60 K followed by a rapid decrease to 0.618 emu mol⁻¹ K at 2.42 K. Complex **2** is EPR silent at 10 K because of the rapid relaxation of $S = 1$ state for Ni(II) and the strong antiferromagnetic interaction between the components of the [Ni(dmit)₂]⁻ dimer. X-ray structural analysis shows that six coordination sites of the nickel atom in the cation are completed with cyclam and solvent molecules and this results in the magnetic isolation of [Ni(cyclam)(CH₃CN)₂]²⁺ from the radicals. Equation 2, which

$$\chi_m = \frac{2Ng_{Ni}^2\beta^2}{3kT} + \frac{Ng^2\beta^2}{kT}\left[\frac{2}{3 + \exp(-2J/kT)}\right] + N\alpha \quad (2)$$

is the sum of the Curie and Bleaney–Bowers equation for [Ni(cyclam)(CH₃CN)₂]²⁺ and the [Ni(dmit)₂]⁻ dimer, respectively, was applied to analyze the magnetic susceptibility data of **2**. The data above 70 K were fit, and this gave $J = -125.4(8)$ cm⁻¹ for the [Ni(dmit)₂]⁻ dimer, $g_{Ni} = 2.160(4)$, and $g = 2.150(2)$, where 200×10^{-6} emu/Ni for $N\alpha$ value was used.

[Cu(cyclam)]₂[2,5-DM-DCNQI]₅ (3). $\chi_m T$ value for **3** gradually decreases from 1.10 emu mol⁻¹ K at 269.0 K to 1.05 emu mol⁻¹ K at 100 K, and then the $\chi_m T$ values do not change down to 10 K followed by a sudden decrease. As stated in the structural study of **3**, there are two kinds of copper complexes and three kinds of DCNQI molecules (**A**, **B**, and **C**). Although the conformers **A** and **B** coordinate to the copper atoms, the magnetic interaction between the copper atoms and **A** or **B** must be negligible because a Jahn–Teller distortion of the copper atom (Cu–N bond lengths are 2.410(3) and 2.502(3) Å for **A** and **B**, respectively) makes the axial bond weak. EPR measurement at 15 K showed an axially symmetric pattern ($g_{\parallel} = 2.169$ and $g = 2.043$) for the copper atom and a small signal ($g = 2.0$) which might be due to a paramagnetic impurity. The EPR result confirms the fact of the magnetic isolation of [Cu(cyclam)]²⁺ from the radicals. Sites **B**'s and **C** form a trimer where interplanar distances are in the range 3.03–3.18 Å. Some anion radical salts of DCNQI series have been reported to be metallic down to a very low temperature. Such conductors have the same ranges of interplanar distances as **3**, and their stacking mode is a "ring over bond" type, which is the same type as **3**. It can be concluded that two spins on the trimer (**BCB**) are strongly coupled to be diamagnetic. Gradual increase of $\chi_m T$ values as the temperature is raised is thought to be due to the DCNQI dimer (two **A**'s) with interplanar distances of 3.71 Å, and this magnetic behavior allowed an estimate of J < −400 cm⁻¹ for the dimer.

Conclusion

Construction of a three-dimensional network, which has a strong magnetic interaction between components, is indispensable to realize molecular based ferromagnets. In this work, [Ni(dmit)₂] and [2,5-DM-DCNQI], which are inorganic salts known to be organic conductors, were used to build multidimensional networks having paramagnetic metal complexes as components. In [M(cyclam)(CH₃CN)₂][Ni(dmit)₂]₂ (M = Cu, Ni), the cations are magnetically isolated, while the anions form a dimer with strong antiferromagnetic interaction ($J = -153(2)$ and $-125.4(8)$ cm⁻¹ for **1** and **2**, respectively). In [Cu(cyclam)]₂[2,5-DM-DCNQI]₅ (3), the paramagnetic metal complex [Cu(cyclam)]²⁺ was successfully incorporated into the radical network; that is, [Cu(cyclam)]²⁺ links the one-dimensional chains of 2,5-DM-DCNQI molecules to form a two-dimensional network. The magnetic interaction of [Cu(cyclam)]²⁺ with paramagnetic 2,5-DM-DCNQI and between [Cu(cyclam)]²⁺ molecules through 2,5-DCNQI molecules are negligible because the Jahn–Teller distortion of the copper atoms (d⁹ configuration) makes the metal–radical bonds weak. A paramagnetic metal complex whose

magnetic orbitals point to the coordinating atom of the organic radicals should be introduced in order to have a magnetic interaction between metal sites and radicals.